Soft-x-ray-induced spin-state switching of an adsorbed Fe(II) spin-crossover complex

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Abstract

For probing the nature of spin-state switching in spin-crossover molecules adsorbed on surfaces, x-ray absorption spectroscopy has emerged as a powerful tool due to its high sensitivity and element selectivity in tracing even subtle electronic, magnetic, or chemical changes. However, the x-rays itself can induce a spin transition and might have unwanted influence while investigating the effect of other stimuli such as temperature or light, or of the surface, on the spin switching behaviour. Herein, we present the spin switching of an Fe(II) complex adsorbed on a highly oriented pyrolytic graphite surface with particular emphasis on the x-ray-induced switching. For a submonolayer coverage, the complex undergoes a complete and reversible temperature- and light-induced spin transition. The spin states are switched both ways by x-rays at 5 K, i.e. from the high-spin state to the low-spin state or *vice versa*, depending on the relative amount of each species. Furthermore, we quantify the fraction of molecules undergoing soft x-ray-induced photochemistry, a process which results in an irreversible low-spin state component, for a particular exposure time. This can be greatly suppressed by reducing the beam intensity.

(Some figures may appear in colour only in the online journal)

1. Introduction

The sensitivity of spin-crossover (SCO) complexes to external perturbations, and hence the ability to control and switch reversibly the spin between the high-spin (HS, paramagnetic) state and the low-spin (LS, diamagnetic or less paramagnetic) state by stimuli such as temperature, light, or pressure [1–4] has fascinated researchers not only for the quest in understanding the fundamental physics involved in the spin-switching process, but also for their potential applications as building blocks in fabricating molecule-based devices, such as in molecular spintronics [5–11]. SCO complexes consist of a central transition metal ion (commonly Fe(II)) with electronic configuration $3d^4$–$3d^7$ ($3d^6$), surrounded by organic ligands. The metastable nature of SCO complexes in the two

spin states stems from the interplay between the ligand field, which favors the LS state, and the spin pairing energy, which favors the HS state.

Device fabrication based on SCO complexes requires their adsorption on a surface, and therein lie the basic challenges (as far as the device integration is concerned): (a) the scarcity of SCO complexes capable of existing in the thin-film form acts as a bottleneck to progress in the field; i.e. over the years, only a few SCO complexes were reported to be vacuum-evaporable [12–16]; (b) the sensitivity of the spin to stimuli can be a double-edged sword: on the one hand, it allows the control and manipulation of the spin state, while on the other, this very property can result in undesirable effects such as a partial or a complete loss of spin-state switchability upon adsorption on a surface. Indeed, the loss of SCO property

or the coexistence of both spin states at all temperatures has been found to be quite a common phenomenon for SCO complexes in contact with surfaces such as Au(1 1 1) [17–20], Bi(1 1 1) [21], Cu(1 0 0) & Cu(1 1 1) [22, 23], highly oriented pyrolytic graphite (HOPG) [24, 25] with the notable exception of two SCO complexes, [Fe^{II}(NCS)$_2$L] (L: 1-6-[1,1-di (pyridin-2-yl)ethyl]-pyridin-2-yl-N,N-dimethylmethan-amine) [26] and [Fe(H$_2$B(pz)$_2$)$_2$(phen)] (hereafter referred to as Fe(bpz)-phen) [27] on an HOPG surface, where a complete spin-state switching by temperature in the former, and by both temperature and light in the latter were reported.

Herein, we report on the temperature, light, and x-ray-induced spin-state switching of 0.8 ML (monolayer) of [Fe(H$_2$B(pz)$_2$)$_2$(bipy)] (hereafter referred to as Fe(bpz)-bipy), deposited on an HOPG surface with a particular emphasis on the x-ray-induced switching, using x-ray absorption spectroscopy (XAS). XAS is a global surface technique, but it has proven to be quite successful in probing the microscopic properties of an SCO complex in contact with a surface, especially when it is used in conjunction with scanning tunneling microscopy (STM). This can be ascribed to two reasons: on the one hand, the high sensitivity and the element selectivity of XAS [28] enables one to probe the electronic states of a submonolayer coverage (isolated molecules) on surfaces vis-à-vis the molecule in the bulk to infer its stability and to pin-point the fragments, if any [17], and on the other, the L_3 edge XA spectral shape of the central metal atom is a unique signature of whether the complex is in the HS or in the LS state [27, 29]. Even in cases where the SCO complex exists in mixed states, it is possible to assign the spin fractions from the L_3 edge XA spectral shape [21].

However, the XAS technique is not without problems: the x rays itself can cause spin-state switching from the LS to HS state at low temperatures, a phenomenon termed as soft-x-ray-induced excited spin state trapping (SOXIESST), or also degrade the complex through soft-x-ray-induced photo-chemistry (SOXPC) [30]. Ever since its first observation on the bulk Fe(phen)$_2$(NCS)$_2$ complex by Collison *et al* [30], and an attempt to shed more light on its dynamic behavior in the same system [31], including the reports in other SCO complexes [16, 17, 21, 27], there has so far been no comprehensive study of the SOXIESST phenomena for SCO complexes on a surface. Here, we attempt to bridge that gap, by showing that x-rays switch the spin states both ways, i.e., LS → HS (SOXIESST) and HS → LS, which we refer to as reverse-SOXIESST, analogous to reverse-LIESST [2]. We present a model that takes into account the three processes involved in the x-ray interaction with an SCO complex, namely, SOXIESST, reverse-SOXIESST, and SOXPC, while ignoring cooperative effects. We interpret the results qualitatively as soft-x-ray-induced spin-state switching being caused mainly by secondary electrons much in the same way as has been suggested in the case of hard-x-ray-induced excited spin state trapping (HAXIESST) [32]. Furthermore, we show that a reduction in the x-ray intensity greatly minimizes the x-ray induced spin switching.

2. Experimental

The SCO complex Fe(bpz)-bipy is synthesized according to the procedure reported in the literature [33]. The molecule is quite robust in the sense that it is stable against evapora-tion, and in the bulk form, exhibits SCO behavior with light, temperature, and pressure [33, 34]. A high-quality HOPG sub-strate (ZYA) of dimension 12 mm × 12 mm × 2 mm with a mosaic spread angle of 0.4(1)° was purchased from Structure Probe. A clean HOPG surface is prepared by cleaving off the top layers by means of a carbon tape at a cleaving stage main-tained at ∼10^{-7} mbar, before transferring it under vacuum to the sample preparation chamber. The molecular powder is evaporated from a tantalum Knudsen cell at 433 K at a pres-sure of ∼2 ×10^{-9} mbar, with the evaporation rate monitored from the frequency change of a quartz crystal. An estimation of the molecular coverage is obtained from the integrated peak intensity of the Fe L_3 absorption spectrum. A monolayer of the complex is defined as 0.82 Fe ions nm^{-2}. The details of the coverage estimation procedure, by calibrating the XAS signal with STM measurements, have been described else-where [17, 27].

The XAS measurements are carried out *in-situ* at the high-field diffractometer beamline UE46-PGM1 at BESSY II with linearly polarized x rays at the third harmonic of the undulator, with the energy resolution set to ≈150 meV. The photon flux density of the x-ray beam, **I$_0$**, determined with a calibrated photodiode, has the value ≈1 × 10^{11} photons s^{-1} mm^{-2} at the Fe L_3 edge. The spectra are measured by the total electron yield mode, i.e. the sample drain current is recorded as a function of the x-ray energy and normalized *wrt* a gold grid upstream to the experiment, and to the background signal from a clean HOPG substrate, at a pressure of ∼5 × 10^{-11} mbar. The Fe L_3 edge XA spectra are recorded at 54.7° (magic angle) between the surface normal and the *k* vector of the lin-early polarized x rays. At this angle, the XA resonance inten-sities are independent of the orientations of the molecular orbitals. Light-induced spin-state switching is carried out with a green LED of wavelength λ = 520 nm having an optical power of ∼400 mW and a spectral width (fwhm) ∼30 nm. The photon flux density is ∼4.2(8) × 10^{14} photons s^{-1}mm^{-2} at the sample position.

3. Results and discussion

Unless otherwise stated, the Fe L_3 edge XA spectra were recorded by damping the x-ray beam with a ∼3 μm thick Al foil, which reduces the original beam intensity (**I$_0$**) by a factor of 15. This is done so as to limit the x-ray effect while investigating temperature- and light-induced spin switching. Figure 1 shows the Fe L_3 near-edge x-ray absorption fine structure (NEXAFS) spectral shapes of 0.8 ML of the SCO complex Fe(bpz)-bipy adsorbed on an HOPG surface (here-after referred to as 'the sample') at 300 K (black colour) and at 5 K (red colour). The two spectra have distinct patterns: while the former spectrum (at 300 K) has two main peaks at 708.3 and 709.1 eV, the latter spectrum (at 5 K) has a main peak
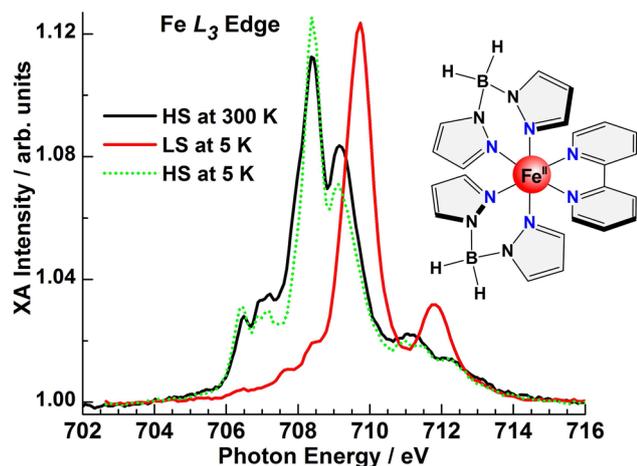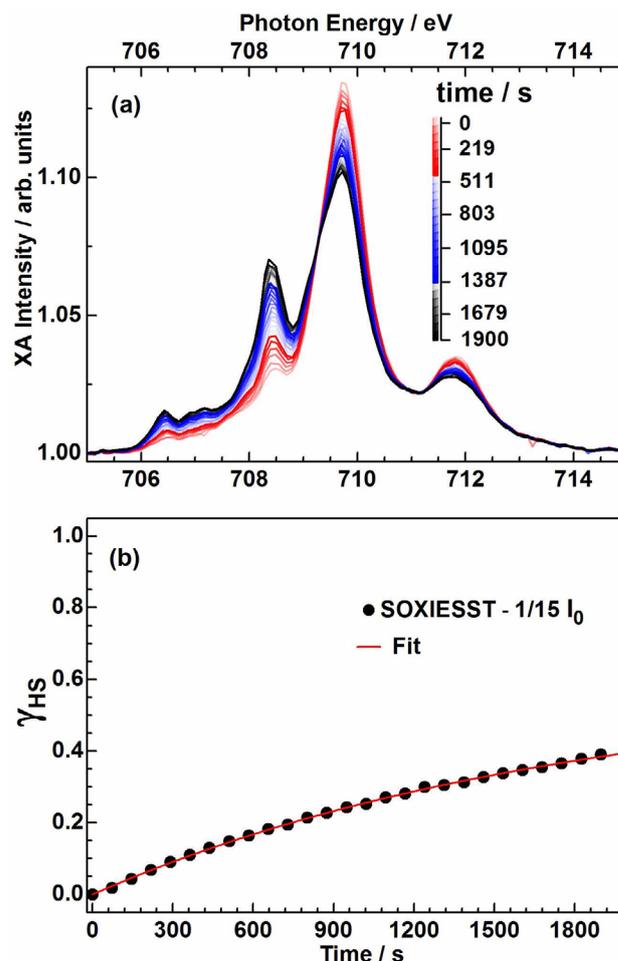
Figure 1. Fe L_3 edge XA spectra of 0.8 ML of Fe(bpz)-bipy on HOPG at 300 K (black line), at 5 K before illumination (red line), and after illumination (green dots) with green light ($\lambda = 520$ nm) at 5 K. Inset: molecular structure of Fe(bpz)-bipy.

at 709.8 eV with a satellite peak at 711.9 eV. These spectral shapes have been established as characteristics of the HS and the LS states, respectively [26, 27, 29].

The temperature-induced spin-state switching displays a behavior similar to that reported for 0.4 ML of Fe(bpz)-phen on the same substrate [27], where the switching process is relatively gradual in comparison to the bulk [33] when cooling from 300 K to 5 K and can be modelled as a system of non-interacting molecules. The sample also exhibits a complete and highly efficient LS → HS switching by irradiating with green light ($\lambda = 520$ nm) at 5 K for ∼50 s, a process termed as light-induced excited spin state trapping (LIESST) [2]. The light-induced pure HS state Fe L_3 spectrum is also shown in figure 1 (green colour).

The Fe L_3 LS spectrum shown in figure 1 (red colour) is the first spectrum recorded for that particular spot on the sample at 5 K, and the spectra recorded successively at that same spot show a gradual build-up of a peak of the HS state at 708.3 eV accompanied with a gradual reduction in the peak intensity of the LS state at 709.8 eV and shifting of this peak towards the other HS state peak at 709.1 eV. This is characteristic of x-ray-induced spin switching from LS to HS state, termed SOXIESST [30].

The SOXIESST phenomenon in SCO complexes is appreciable only at low temperatures, for the sample under investigation, <70 K. As the sample is prone to x-ray-induced switching at 5 K, in order to follow a proper build-up of the HS state by x rays, starting from a pure LS state, the first spectrum of the series is recorded at a virgin spot on the sample, and if there is any trace of a peak (or bump) at 708.3 eV indicative of the presence of x-ray-induced HS state, the temperature is increased to 80 K to obtain the pure LS state and subsequently cooled to 5 K. In any case, if a spectrum shows no bump at 708.3 eV, it is taken as the pure LS spectrum. The time stamp for each spectrum as it is recorded succesively one after the other is taken as the time when the resonance peak (708.3 eV) is reached during the scan. The HS fractions γ_{HS} for each spectrum are estimated from fitting it with a linear combination of the pure HS spectrum and the pure LS spectrum (the
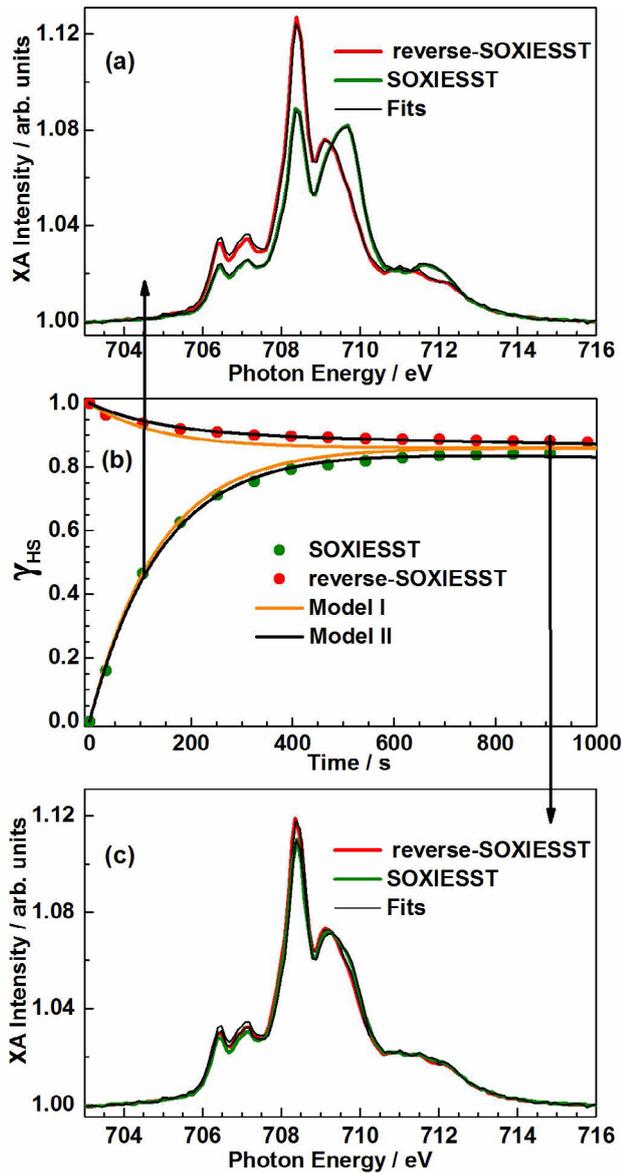

Figure 2. (a) Time evolution of x-ray-induced spin-state switching of 0.8 ML of Fe(bpz)-bipy on HOPG at 5 K traced by the Fe L_3 edge XA spectral change; and (b) the estimated γ_{HS} from the spectra shown in (a) with the fit using model (I). The x-ray beam is damped with a thin Al foil that decreased its intensity by a factor of 15.

first spectrum of the series). The saturated spectrum obtained after ≈5 min exposure to green light is taken as representing the complete (pure) HS spectrum (figure 1 (green dots)). The gradual build-up of x-ray-induced LS → HS conversion is shown in figure 2(a) (spectral form) and figure 2(b) with the γ_{HS} estimated from the procedure described above.

In order to estimate the rate constants of the switching process, a simple model (hereafter referred to as model (I)), LS ⇌ HS, is applied. The differential rate equation of the process can be written as:

$$\frac{d\gamma_{HS}}{dt} = k_{1d}\gamma_{LS} - k_{2d}\gamma_{HS} \quad (1)$$

where k_{1d} and k_{2d} are the rate constants for the transitions LS → HS and HS → LS, respectively (the d in the subscripts stands for 'damped x-ray beam'). Solving the above equation and fitting it with the experimental data by the method of least squares yields the values of k_{1d} and k_{2d} as $3.50(3) \times 10^{-4}$ s^{-1} and $2.3(1) \times 10^{-4}$ s^{-1}, respectively, with the saturation γ_{HS} at ∼0.60(5). This is the x-ray contribution to the switching process while investigating SCO complexes

Figure 3. (b) Time evolution of x-ray-induced spin-state switching of 0.8 ML of Fe(bpz)-bipy on HOPG at 5 K, with an intensity **I₀**. The orange and black lines are the fits from model (I) and model (II), respectively. (a) and (c) represent the Fe L_3 edge XA spectral shapes after x-ray exposure times of 106 s and 900 s, respectively, starting from a pure HS state (red dots, reverse-SOXIESST) and a pure LS state (olive dots, SOXIESST). The black lines are fits of the spectra obtained by the linear combination of the pure HS and LS spectra so as to extract the spin fractions.

at low temperatures, and is highly dependent upon the photon flux, as will be shown in the following. Here, for the damped x-ray beam, the possibility of SOXPC is not taken into account as the pure HS spectrum can be obtained by exposure to light after the SOXIESST series measurements.

Figure 3(b) shows the x-ray-induced spin-state switching with the full photon flux **I₀** (i.e. without damping the beam with Al foil), where the switching occurs in both ways: the so-called SOXIESST (LS → HS), when starting from the pure LS state, represented by the lower curve, and reverse-SOXIESST (HS → LS), when starting from the pure HS state, represented

by the upper curve. It must be mentioned that this is the first report of reverse-SOXIESST. The reverse-SOXIESST measurements are done after the sample has been saturated to the HS state by exposure to green light. Also shown in figures 3(a) and (c) are the Fe L_3 edge XA spectra at two different exposure times to the x-ray beam, marked with arrows (at 106 s and 900 s), and their corresponding fits by a linear combination of the pure HS and LS state spectra.

For a quantitative modelling of the kinetics, in addition to model (I), a second model (hereafter referred to as model (II)), LS ⇌ HS, LS→LS', and HS → LS', is applied. The LS' state refers to the altered and irreversible low-spin component that results from the interaction of the SCO complex in the LS state with the x rays, by a process termed as soft-x-ray-induced photochemistry (SOXPC) by Collison, *et al* [30], who observed this phenomenon for the first time. No related report of this phenomenon is to be found in the literature since then. The origin of SOXPC is still unknown at the molecular level. In SOXIESST, the spin switching saturates at ∼84(5)% HS state while the reverse-SOXIESST process is much slower, attaining about ∼13(5)% switched to the LS state for the same amount of x-ray exposure (figure 3(b)). Incomplete switching by x rays was also reported in bulk Fe(phen)₂(NCS)₂, with saturation at about 90% HS state with a photon flux of 12% of **I₀** [31], while complete switching is reported for the same bulk molecule with a photon flux **I₀** [30], apparently before the onset of SOXPC.

According to model (II), the differential rate equations for each species are given by the following mass balance simultaneous equations,

$$\frac{d\gamma_{LS}}{dt} = -k_{1f}\gamma_{LS} + k_{2f}\gamma_{HS} - k_{3f}\gamma_{LS} \tag{2}$$

$$\frac{d\gamma_{HS}}{dt} = k_{1f}\gamma_{LS} - k_{2f}\gamma_{HS} - k_{4f}\gamma_{HS} \tag{3}$$

$$\frac{d\gamma_{LS'}}{dt} = -\left(\frac{d\gamma_{HS}}{dt} + \frac{d\gamma_{LS}}{dt}\right) \tag{4}$$

where k_{1f}, k_{2f}, k_{3f}, and k_{4f} are the rate constants for the transitions LS → HS, HS → LS, LS → LS', and HS → LS', respectively. (The f in the subscripts stands for 'full photon flux'.) Solving the above differential rate equations simultaneously while satisfying the initial conditions at t = 0, i.e. (i) $\gamma_{HS} = 0$, $\gamma_{LS} = 1$, (SOXIESST) and (ii) $\gamma_{HS} = 1$, $\gamma_{LS} = 0$ (reverse-SOXIESST), and fitting to the experimental data yields the values of the rate constants as $k_{1f} = 6.1(1) \times 10^{-3}\,s^{-1}$, $k_{2f} = 6.5(3) \times 10^{-4}\,s^{-1}$, $k_{3f} = 3.9(4) \times 10^{-4}\,s^{-1}$, and $k_{4f} \to 0$. (The absence of the conversions from HS to LS' is in agreement with that reported in the literature [30].) This gives the SOXIESST effective cross-section ($k_{1f}/\mathbf{I_0}$) as ≈6 Å², which is ≈5.0 × 10² times the effective cross-section of LIESST reported for 0.4 ML of Fe(bpz)-phen on HOPG [27], and about ≈44 times that reported for this complex in thin film [35]. Applying model (I) with the same initial conditions as above fitted quite well with the experimental spin switching rates initially, but deviates with the increase in exposure time, as shown in figure 3(b), (orange curves), which, in other words, confirms the time evolution of the LS' states.

To discuss the mechanism responsible for the observed SOXIESST and reverse-SOXIESST, we first estimate the x-ray absorption rate per molecule. The off-resonant absorption cross-section of an Fe(bpz)-bipy molecule can be calculated as the sum of the tabulated values of the absorption cross sections of its chemical constituents [36, 37] to be 0.050 $\overset{\circ}{A}^2$ at 690 eV. The cross section at resonant absorption at the Fe L_3 edge is typically a factor of 5 to 15 higher than the tabulated cross section edge jump of 0.015 $\overset{\circ}{A}^2$. The estimated absorption rates per Fe(bpz)-bipy molecule in our expriment, as obtained from the product of the cross section and the photon flux density, have values of 0.5×10^{-4} s^{-1} and 2×10^{-4} s^{-1} for the non-resonant and resonant absorption, respectively. These are much lower than the observed SOXIESST transition rates. Hence, we can rule out the possibility of spin switching directly by x-ray absorption in the molecules. On the other hand, the estimated resonant absorption rate is in the same range as the experimentally observed rate of SOXPC, suggesting that direct x-ray absorption in the molecules might indeed be responsible for the photochemistry.

In the case of hard-x-ray-induced spin-state switching reported for the bulk Fe(phen)$_2$(NCS)$_2$ complex [32], the authors attributed secondary electrons originating from a remote ionization as being responsible for the switching process. It can be assumed that the same process applies for SOXIESST as well. Interestingly, no hard x-ray-induced photochemistry (HAXPC) was observed. The reason for the observation of SOXPC and the absence of HAXPC could lie in the possible difference in the SCO complexes' effective cross section to soft and hard x rays.

The dependence of the x-ray-induced spin-state switching on photon energy (i.e. at resonant or non-resonant energy) can provide additional information on the underlying mechanism. If, for example, SOXIESST were due to direct excitation of the molecules by x-rays, one would expect to see a large difference in the switching rates for illuminations at resonance (709.8 eV) or off-resonance (say, 690.0 eV) x-ray energies, paralleling the difference in resonant and non-resonant absorption cross section. To test this, two x-ray-induced switching rates (starting from the pure LS states) are recorded by illuminating the sample at resonance photon energy (709.8 eV) and off resonance (690.0 eV). For both series, the sample is exposed alternatingly to the monochromatic x-ray beam with full photon flux, and to an attenuated x-ray beam for recording the spectra. The time evolution of γ_{HS} for both series is shown in figure 4 ($\square$ and $\triangle$ for 709.8 and 690.0 eV, respectively). By using model (I) and ignoring SOXPC for simplicity, the time evolution of γ_{HS} induced both by monochromatic x-ray exposure and that during recording the spectrum has a solution of the form:

$$\gamma_{HS}(\Delta t_1, \Delta t_2) = \frac{e^{-(k_{1d}+k_{2d})\Delta t_1 - (k_{1m}+k_{2m})\Delta t_2}}{(k_{1d}+k_{2d})(k_{1m}+k_{2m})}$$
$$\times [e^{(k_{1d}+k_{2d})\Delta t_1}(k_{1d}k_{2m} - k_{2d}k_{1m}$$
$$+ e^{(k_{1m}+k_{2m})\Delta t_2}k_{1m}(k_{1d}+k_{2d}))$$
$$+ (k_{1m}+k_{2m})(k_{1d}(\gamma_{HS0}-1) + k_{2d}\gamma_{HS0})]$$

$$(5)$$
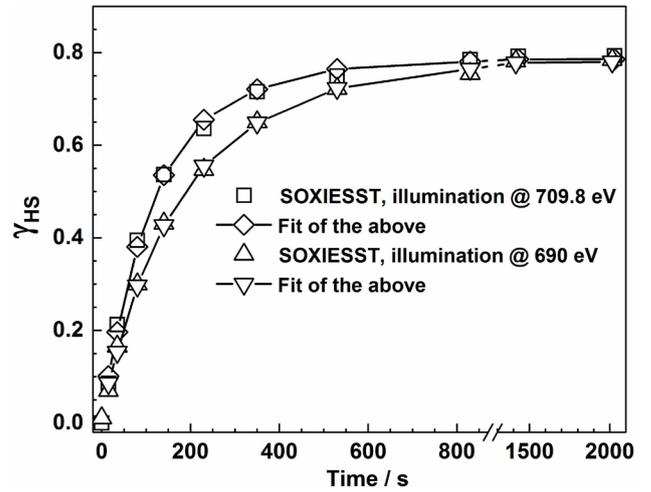
Figure 4. Time evolution of SOXIESST upon illumination with two different photon energies: at resonance (709.8 eV), $\square$, and at off-resonance (690.0 eV), $\triangle$. Also shown are the fits based on model (I), $\diamond$ and $\triangledown$.

where Δt_1 is the time it takes to record one spectrum, which is ~73 s, Δt_2 is the discrete exposure time to the unattenuated monochromatic x rays, and γ_{HS0} is the HS fraction before every consecutive exposure to the x rays. The rate constants k_{1d} and k_{2d} have the same meaning as in equation (1), while k_{1m} and k_{2m} are the rate constants for the transitions LS $\rightarrow$ HS and HS $\rightarrow$ LS induced by monochromatic x rays, respectively. Substituting the value of the rate constants k_{1d} and k_{2d} obtained from equation (1) into equation (5) and fitting it with the experimental data of figure 4 by the method of least squares, the following values are obtained for the rate constants: $k_{1m} = 5.5(3) \times 10^{-3}$ s^{-1} and $k_{2m} = 1.5(1) \times 10^{-3}$ s^{-1} on illumination with x-ray energy at resonance (709.8 eV) and $k_{1m} = 3.6(2) \times 10^{-3}$ s^{-1} and $k_{2m} = 1.02(7) \times 10^{-3}$ s^{-1} for the off-resonance (690.0 eV) illumination. The probabilities of LS $\rightarrow$ HS transitions, $k_{1m}/(k_{1m}+k_{2m})$, and HS $\rightarrow$ LS transitions, $k_{2m}/(k_{1m}+k_{2m})$, are remarkably similar in both cases; i.e. ~0.79 and ~0.21, respectively.

The difference in the rates of about 50% between resonant and off-resonant illumination is clearly smaller than the difference in absorption, thus also ruling out a direct optical excitation of the molecules as responsible mechanism for SOXIESST. At the resonance x-ray energy, the photocurrent, and thus the number of emitted secondary electrons, is higher by only about 12% than at the off-resonance energy. These 12% additional secondary electrons, however, are generated in the molecular layer and may thus have a higher probability of interacting with the molecules than the electrons originating from the substrate. This could account for the about 50% higher rate constants at the resonance as compared to the off-resonance case. This argument is supported by the report of a similarly high rate constant for SOXIESST as ours for a bulk SCO complex, but obtained with a much reduced photon flux (about 12% of our I_0) [31]. This is consistent with more efficient switching when all the secondary electrons originate from the complex itself.

Electron-induced excited spin state trapping (ELIESST) has been reported for a bilayer of Fe(bpz)-phen on Au(1 1 1),

studied by STM: the LS to HS transition is observed by applying a sample voltage in the range of 2.5–3.0 V with the STM tip positioned at a nanometer above the molecules, and a HS to LS transition is observed when the sample voltage is maintained in the range of 1.6–1.8 V and the current strongly increased [19]. The authors suggest that the LS $\rightarrow$ HS spin transition occurs via a mechanism where electrons are injected into the unoccupied orbitals that excite the LS molecule to LS$^-$, followed by a relaxation to an intermediate state I$^-$, which then statistically relaxes to the HS or LS states. This is further corroborated by a DFT calculation that showed that for LS molecules, the energy difference between HOMO and LUMO is $\sim$2.1 eV [19]. We propose a similar mechanism for SOXIESST: for the LS molecule, the injection of the x-ray-induced secondary electrons to the unoccupied orbitals leads to a weakening of the Fe–N coordination bond. Consequently, the bond lengthens, resulting in a reduction of the ligand field strength. When the electron hops off, the molecule relaxes statistically to the HS and the LS states. For the electron-induced HS $\rightarrow$ LS transition, on the other hand, the strong injection of electrons of energy 1.6–1.8 eV to the sample was needed [19]. This energy is in the same range as that of the energy difference between $^5T_2$ and ^5E states. Therefore, one cannot rule out the possibility of x-ray-induced HS $\rightarrow$ LS spin-state switching occurring via intersystem crossing, through the inelastic scattering of secondary electrons.

The observed SOXIESST and reverse-SOXIESST effects are phenomenologically similar to LIESST and reverse-LIESST. Since its first observation by Decurtins *et al* [38], the LIESST process in SCO complexes has been well investigated and understood as being due to the intersystem crossing that involves the excitation of electrons from the electronic ground state ($^1A_1$, LS state) to the metal-to-ligand charge transfer states (^{1,3}MLCT), from whence the electrons undergo fast decay to the quintet ligand field state ($^5T_2$, metastable HS state) via the low-lying triplet ligand field excited states (^3T). Conversely, the reverse-LIESST process can be carried out by irradiation in the near-IR region, whereby the electrons in the $^5T_2$ HS state are excited to the ^5E ligand field state, from whence they relax to the $^1A_1$ LS state, although it is not as efficient as that of LIESST because of the large overlap between the ^5E and $^5T_2$ states [2]. The time constants for every step involved in the process have been probed in detail by ultrafast optical and x-ray spectroscopies [39, 40]. The reverse-SOXIESST process is relatively slow, similar to the reverse-LIESST process. In the reverse-LIESST process, this is attributed to the large overlap between the HS state ($^5T_2$) and the excited state (^5E). (The electrons excited to the ^5E state have a high probability to relax back to the $^5T_2$ state, apart from undergoing intersystem crossing.) A similar effect of soft-x-ray and optical near-IR irradiation as in SCO complexes (HS $\rightarrow$ LS) has also been reported in another class of molecules, namely cobalt dioxolene, which undergoes redox isomerism both with soft-x-ray and optical near-IR irradiations [41]. As mentioned before, however, our effective cross section for SOXIESST is much higher than that of LIESST, consistent with the interpretation that the transition is induced by secondary electrons rather than by direct optical excitations of the molecule's electronic

states. The secondary electrons' energy versus intensity distribution from various conducting surfaces, induced by x rays of the energy range 100–10 000 eV, are fairly similar and can best be described as a convolution of two exponential decays or of a Gaussian and an exponential decay, having maximum intensity in the region of $\sim$1–2 eV [42]. These electrons could then induce the spin-state switching, similarly to ELIESST, by injection into unoccupied molecular orbitals for LS $\rightarrow$ HS and by an excitation of the molecule's electronic system by inelastic scattering for the HS $\rightarrow$ LS transition.

4. Conclusion

[Fe(H$_2$B(pz)$_2$)$_2$(bipy)]-HOPG is a promising system for further exploration with a view for potential device fabrication, as the spin-state switching process is seemingly unhindered by the surface, unlike any other surfaces explored so far for the complex. As suitable as XAS may be for investigating SCO complexes on surfaces, both the x-ray-induced molecular alteration and spin-state switching at low temperatures renders the technique potentially complicated. However, this issue can be largely overcome by making a judicious choice of the photon flux, as has been shown by us in this study, and by others elsewhere [16]. We have attempted to explain both quantitatively and qualitatively the mechanisms of soft x-ray and SCO–molecule interaction: quantitatively with a model that takes into account all the processes involved, and qualitatively on the basis of secondary electrons arising mainly from the substrate as being responsible for both the SOXIESST and reverse-SOXIESST phenomena.

Acknowledgments

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